Tunable cobalt nanoparticle synthesis by intense pulse flash annealing

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Magnetically susceptible materials can serve as a basis for the directed assembly of nanoscale network devices which can be used to extract energy from phase change materials. So far, matrix production cost has been a prohibitive factor in the realization of real world applications. Here we report a cost-effective method to synthesize magnetic nanoparticles. Samples were fabricated by sputtering magnetic thin films on carbon nanotube substrates followed by xenon intense pulsed light flash annealing. The results indicate that spatially ordered magnetic spheres can be tuned by various parameters such as initial thin film thickness, xenon lamp exposure excitation energy, local surface geometries, and the presence of an external magnetic field during annealing. © *2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* [http://dx.doi.org/10.1063/1.4975044]

I. INTRODUCTION

Metallic nanoparticle arrays which exhibit magnetic moments are a promising platform for the production of electrically and thermally conductive micro- and nanoscale structures. Real world applications include fields such as biomedical engineering, data storage, and non-linear optics.[1,2] In order to capitalize on major natural energy sources; such as solar and wind energies, efficient methods of energy storage must be developed. Recently, attention has been given to Latent Heat Storage (LHS) devices which utilize Phase Change Materials (PCMs) due to their low cost, low toxicity, and high engineering versatitlity as candidates for efficient, cost-effective methods of thermal energy storage.[3,4] One promising work to develop an LHS device utilizes paraffin as a PCM and incorporates a matrix of magnetically susceptible, thermally conductive nanorods which are self-assembled by using a microscaled array of magnetic pads. The assembly process to create the matrix is well documented, however the prohibitive cost of the magnetic pads, fabricated by lithography processes, makes large-scale production impractical.[5–7]

Planar thin films are susceptible to a dewetting instability in which a continuous film spontaneously decomposes into an equilibrium morphology of discrete shapes having characteristic size.[8] This process, known as agglomeration, is primarily a surface energy driven phenomenon, and is best understood through the thermodynamics of energy minimization.[8–12] During the agglomeration process, void nucleation occurs at various sites throughout the thin film as a result of stress, strains, defects, structures which protrude up into the thin film from the substrate, or preexisting voids which exceed a critical radius. As nucleation proceeds, laminar flow of mass away from the void edges will cause fingers of the material to form. Eventually, Rayleigh instabilities cause breakup of these fingers into discreet islands of hemispherical, or near spherical equilibrium shapes, which completes the thermodynamic transition.[11,13,14]

Here we examine the self assembly of nano arrays of cobalt nanospheres synthesized by solid state dewetting on low surface energy carbon nanotube substrates with non-trivial local geometry. Solid

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state dewetting by Intense Pulsed Light (IPL) flash annealing is an easily repeatable morphological process, driven by thermodynamic and hydrodynamic principles, which utilizes a simple experimental setup, providing a navigable roadmap to the creation of magnetically susceptible, tunable nanoparticle arrays.[15] We found that the dimensions of end state equilibrium shapes after agglomeration in our thin film-substrate system are highly parameter dependent.

II. EXPERIMENT

The carbon nanotube substrates used in our study consisted of two types: an in-lab made drop cast type, and a Buckypaper as supplied from NanoTech Labs Inc. The in-lab substrate was made by dispersing 5mg of M-grade multi-walled carbon nanotubes into 20mL of acetone, subjecting this mixture to 80 minutes of sonic agitation, and then drawing the mixture into a pipette and applying to a silicon wafer. After a short time period, the acetone evaporated leaving behind a film of carbon nanotubes. The second type of substrate was a proprietary nanotube mesh or Buckypaper comprised of a dense matrix of multi-walled carbon nanotubes with diameters ranging from 5-80nm. In order to facilitate handling and characterization by scanning electron microscopy, the Buckypaper was glued on silicon wafers with silver conductive paste.

Direct current magnetron sputtering deposition in an inert argon atmosphere was used to prepare cobalt thin films with different initial film thicknesses on the carbon nanotube substrates. Deposition rate was measured to be $1\frac{nm}{min}$ by a single crystal quartz thickness monitor and this was verified with measurements by atomic force microscopy. Base pressure was maintained at 10^{-7}Torr with argon gas introduced at 40mTorr and a sputtering target with purity of 99.95% cobalt was used.

Solid state dewetting of the thin film samples was achieved by using IPL flash annealing. The excitation source was a commercially available system consisting of an adjustable output capacitor bank and a xenon flash bulb capable of energies up to $50\frac{J}{cm^2}$ on time scales ranging from 1 to 30ms. For this study, all excitation energy exposures were 20ms. Scanning electron microscope characterization was done using a Jeol 7800F FESEM. The conductive nature of the carbon nanotube substrate and the nanoparticles allowed for crisp imaging with no distortion due to charging effects.

III. RESULTS AND DISCUSSION

The choice of carbon nanotubes for a substrate is due to the low surface energy[16] and high aspect ratio geometry of carbon nanotubes. The best results were obtained using a proprietary multi-walled carbon nanotube Buckypaper produced by NanoTech Labs Inc. High thermal conductivity, mechanical robustness, and chemical stability[17] of carbon nanotubes makes them suitable candidates for use in PCM/LHS devices. Solid state dewetting with a xenon IPL flash lamp facilitates dewetting on a short time scale, and does not destroy the underlying substrate. We found that the dimensions of end state equilibrium shapes after agglomeration in our thin film-substrate system are highly parameter dependent. The main process parameters studied in this work are initial thin film thickness $h_\circ$, excitation energy, and the presence of an applied magnetic field.

After exposure to excitation energy, SEM images revealed a boundary which separates the area populated with nanoparticles from an area without dewetting, as shown in Figure 1. Since the homogeneous exposure area of the light source is not as large as the surface area of the sample, this sharp transition boundary indicates a threshold energy for dewetting. The nature of our experimental setup is such that the excitation source cannot fully cover the total surface of the substrate, therefore leaving a "strip" of nanoparticles bordered by a transition area separating a nanoparticle-populated region from a region where the thin film is still continuous and in an un-agglomerated state. This can provide insight into a proper, developed theory for solid state dewetting on cylindrical surfaces of high aspect ratio.

In order to determine the relationship between excitation energy and end state particle size, a series of samples was tested for each type of substrate, with energies progressing from $10\frac{J}{cm^2}$ to $40\frac{J}{cm^2}$ and initial thin film thickness of $h_\circ$=20nm. ImageJ software was used for analysis of the micrographs and, as shown in Figure 2, a systematic change in particle size was observed where average particle size of 44.7nm, 46.2nm, 54.8nm, and 63.7nm corresponded to excitation energies of $10\frac{J}{cm^2}$, $20\frac{J}{cm^2}$,

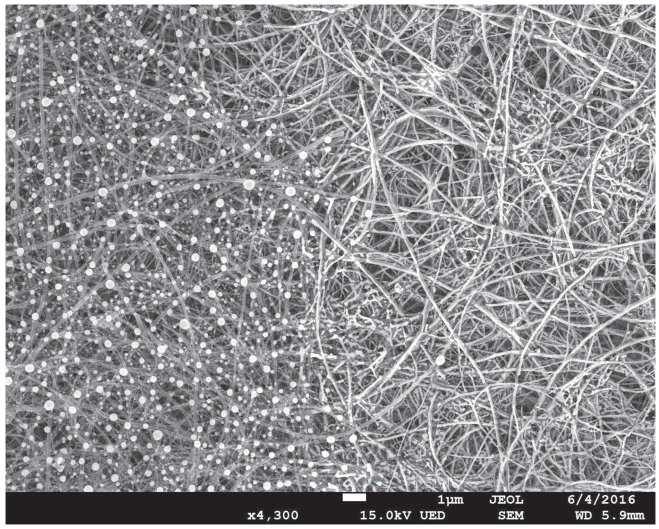

FIG. 1. Clear line of demarcation between continuous thin film and agglomerated nanoparticles indicates a threshold energy. Initial cobalt thin film of nominal thickness $h_\circ$=20nm and excitation energy of $50\frac{J}{cm^2}$, scale bar indicates 1μm size.

$30\ \frac{J}{cm^2}$, $40\frac{J}{cm^2}$. The progressively larger size is a result of accelerated process due to absorbed energy, resulting in Ostwald ripening of the particles.[18] These observations agree with theoretical models and other experiments.[15,19] Visual inspection of the micrographs shows a consistent correspondence between excitation energy and particle size. Higher excitation energies correspond to higher surface temperatures. Diffusivity is a temperature-dependent quantity,[12] therefore increased diffusivity would mean increased mass flux, and increased flux would allow for the evolution of the agglomeration process to proceed into the Ostwald ripening stage. Ostwald ripening accounts for the shift to larger particles and hence the absence of smaller ones, as the smaller particles are subsumed by their larger neighbors.

Initial thin film thickness was varied for two series of samples with $h_\circ$ ranging from 10nm to 20nm in 5nm increments. As shown in Figure 3, in both cases a systematic reliance on the initial parameter $h_\circ$ is observed. Given that the surface curvature of the edge of a void or nucleation site goes as the inverse of its radius, the radius being equal to $h_\circ$, it follows that surface diffusion flux, and therefore agglomeration propagation, is reliant on $h_\circ$. These observations again confirm that the planar agglomeration model is a good baseline. It has been well documented in the literature that initial thin film depth plays a role in both susceptibility to agglomeration as well as end state particle size for planar surfaces.[8] For our surface, comprised of a local geometry possessing high aspect ratio, similar results are observed. The role of initial thin film depth is observed on the in-lab made multi-walled carbon nanotube substrates; however the more uniform particle distribution present on the buckypaper substrate clearly shows the reliance on $h_\circ$. The higher density of carbon nanotubes on the Buckypaper creates an topography which approaches a continuum which contributes to the uniform distribution of end state structures. It has been documented that

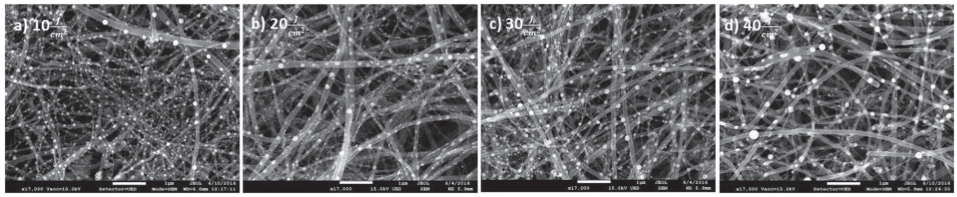

FIG. 2. Cobalt nanoparticles fabricated from thin film of nominal thickness 20nm, by flash lamp annealing on drop-cast CNT substrate using a range of excitation energies: a)$10\frac{J}{cm^2}$, b)$20\frac{J}{cm^2}$, c)$30\ \frac{J}{cm^2}$, d)$40\frac{J}{cm^2}$. Scale bar is 1μm for all SEM images.

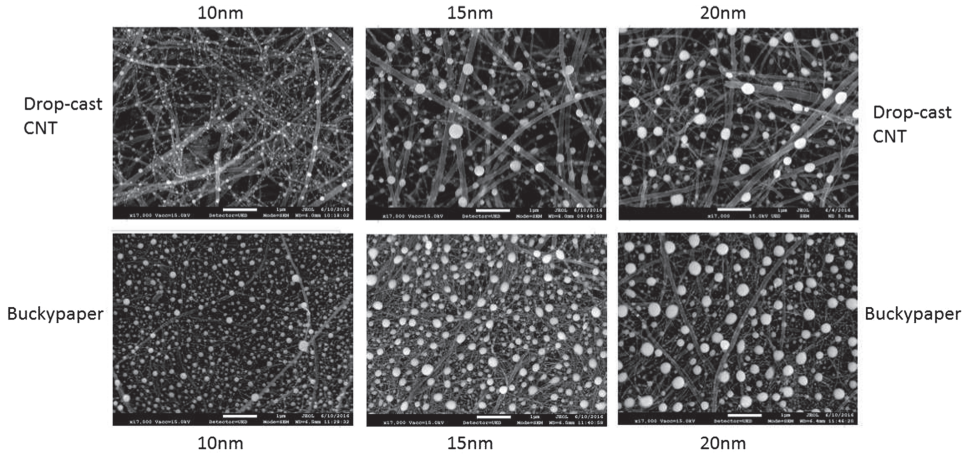

FIG. 3. Substrate comparison. Top row, cobalt on drop-cast CNT. Bottom row, cobalt on $60\frac{g}{m^2}$ Buckypaper. Initial film thickness from left to right $h_\circ$=10nm, 15nm, 20nm. All samples had excitation energy of $50\frac{J}{cm^2}$. Scale bar is 1μm for all SEM images.

reflectivity of base substrates plays a major role in producing the thermal conditions necessary for agglomeration.[20] The drop cast substrates are less dense than the Buckypaper, and therefore reflectivity of the underlying silicon wafer plays a stronger role in the temperature during annealing. Figure 3 shows a noticeable jump in particle size between 10nm and 15nm initial thin film thickness.

The initial thin film thickness, $h_\circ$, was varied on a series of cobalt-on-Buckypaper samples, and annealed at $50\frac{J}{cm^2}$ in the presence of an external magnetic field of magnitude 830 Gauss. In comparison to samples of varied thickness also annealed at $50\frac{J}{cm^2}$, without magnetic field present, the samples with an external applied magnetic field present during annealing, exhibited nominally larger particles as shown in Figure 4. The magnetic properties of cobalt may assist in diffusion during Ostwald ripening, causing a dipole-dipole interaction which may extend the effective Ostwald range. These results point to the further tunability of this process and warrant further study into the role magnetic susceptibility could play. For all samples, flash annealing in ambient conditions introduces oxygen, and therefore cobalt oxide may be produced along with cobalt nanoparticles. Preliminary XRD analysis indicates that pre-treatment cobalt thin film as well as end state particles are crystalline. Further work will provide more comprehensive specific composition and phase details.

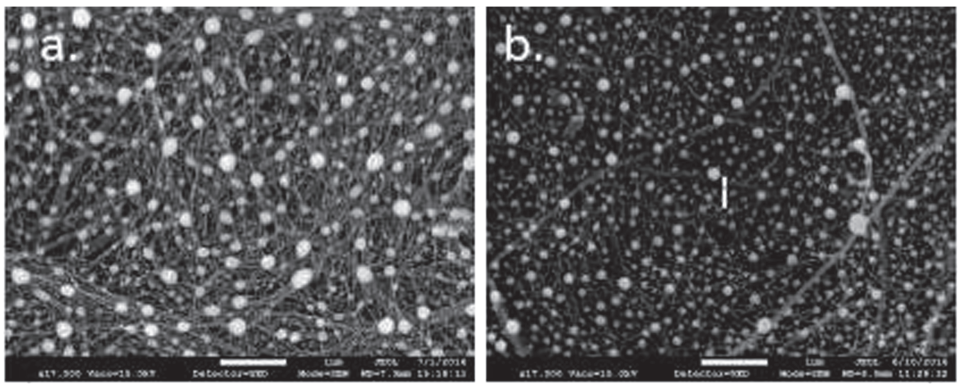

FIG. 4. Comparison of particles made with and without magnetic field present: a) annealed with magnetic field of 830G, and b) annealed without magnetic field. Both samples had initial thin film thickness of $h_\circ$=10nm and excitation energy of $50\frac{J}{cm^2}$. Scale bar is 1μm for all SEM images.

IV. CONCLUSIONS

We have demonstrated that the solid state dewetting of cobalt thin films on carbon nanotube substrates is a highly tunable, easily repeatable process to fabricate nanoparticle arrays. The short time scale and relatively low energetics involved make this method a suitable candidate for roll to roll production or as an inexpensive platform for research. It was shown that density of the underlying carbon nanotube foundation, initial thin film thickness, excitation energy, and application of an external magnetic field are all parameters that can be used to adjust end state structure. Transition areas indicate a threshold energy, or temperature, present in solid state dewetting. These observations fell in line with expectations upon the consideration of models designed for a planar geometry agglomeration processes.

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